**Supplementary Material**

**Determination of fossil fuel component in atmospheric CO2**

The atmospheric CO2 at a given location may originate from various sources (e.g. Levin et al. 2003, Turnbull et al. 2009; Zimnoch et al. 2004; Vogel et al. 2013; Graven and Gruber 2011, Graven et al. 2018): a natural component, for undisturbed, "clean air" (so-called background); a biospheric component, resulting from the ecosystem uptake and respiration (CO2bio); a fossil component, caused by fossil fuels combustion (CO2fossil); a nuclear component in the vicinity of nuclear infrastructure, where an excess 14C is produced (CO2n); a component associated with ocean exchange (CO2o); a stratospheric component (CO2s). The CO2 composition gives the mass balance equation:

CO2meas = CO2bg + CO2bio + CO2fossil + CO2n + CO2o + CO2s (1),

There is no nuclear infrastructure nearby our study site, no ocean influence, and no meaningful stratosphere CO2 present near the Earth’s surface. Thus, we assume for our interpretation of measurement results that the local atmospheric CO2 near the ground level in Gliwice (CO2meas) consists of three components: background CO2, representing the regional atmosphere not influenced by local sources of carbon dioxide, (CO2bg), the local biogenic component representing contributions from the biosphere (CO2bio), and the local fossil fuel combustion component (CO2fossil). Under this assumption the mass and isotope balance equations can be formulated as (Levin et al. 2003, Zimnoch et al., 2004):

CO2meas = CO2bg + CO2bio + CO2fossil  (2),

CO2meas∙(Δ14Cmeas +1000)= CO2bg ∙ (Δ14Cbg +1000) +

+ CO2bio ∙ (Δ14Cbio +1000) + CO2fossil ∙ (Δ14Cfossil +1000) (3).

For CO2fossil the value of Δ14C = -1000‰, because the 14C/12Cfossil ratio is zero. Also, in the case of the current research we follow Levin et al. (2003) assuming that the major flux from the biosphere comes from autotrophic respiration, a young reservoir in very close 14C equilibrium with atmospheric CO2. Therefore, we assume that:

Δ14Cbio = Δ14Cmeas (4).

Combining the equations 2, 3 and 4 the ratio of CO2foss to the total CO2 measured in the air (CO2meas) can be determined as FFCO2, which is a measure of the local Suess effect, expressed as a percentage value:

$FFCO\_{2}=\frac{CO\_{2fossil}}{CO\_{2meas}}=\frac{∆^{14}C\_{bg}-∆^{14}C\_{meas}}{∆^{14}C\_{bg}+1000}∙100\%$ (5).

**Earlier Suess effect investigations for Southern Poland**

For the city of Gliwice and several other sites from the Silesian agglomeration, systematic radiocarbon determinations of the fossil fuel component in atmospheric CO2 were made in the years 1980-1984 (Awsiuk and Pazdur 1986). Atmospheric CO2 samples collected in January 1974 (1 sample) and in 1980–1984 (5 years, average of 8 samples/year) were collected by absorption in NaOH for 1 week. Awsiuk and Pazdur (1986) investigated the variability of the Suess effect and its spatial distribution and dependence on meteorological conditions.

For the two cities of the Silesian agglomeration, i.e. Ruda Śląska and Chorzów, the Suess effect was investigated by 14C isotope measurements using tree rings of *Pinus Sylvestris* L. and *Populus nigra* L. for the years 1965-1995 (**Rakowski et al. 2001**). Radiocarbon measurements were performed using Liquid Scintillation Counting (LSC), with a 5-year resolution.

The first investigations into isotopes 14C and 13C for the city of Krakow, located about 100 km east of the Silesian agglomeration (Fig. 1), were carried out using plants by Florkowski and Kuc (1979). Detailed studies were made for atmospheric CO2 (Kuc et al. 2007, Zimnoch et al. 2012, 1-month time resolution) by LSC and in annual tree rings (Rakowski et al. 2004, 1-year time resolution) by Accelerator Mass Spectrometry (AMS). The period of research covered the last dozen or so decades, i.e. the period of the industrial development of Poland. The 14C and 13C isotope measurements were primarily modeled to determine the reduction of the 14C concentration in the atmosphere due to the combustion of fossil fuels. In the case of Krakow, based on the model, the value of the biogenic component was estimated (Zimnoch et al. 2012).

*Pinus Sylvestris* L. tree rings from Niepołomice Forest, ca 15 km E from Krakow were investigated as part of the EU-funded ISONET project (“400 years of Annual Reconstructions of European Climate Variability using a High Resolution Isotopic Network”; Treydte et al. 2007). Additional AMS 14C studies have been performed on the same material (Pazdur et al. 2007; Rakowski et al. 2010). The results have been incorporated into the compilation curve used for the calibration of radiocarbon results by Hua et al. (2013).

A detailed summary of the results of the above studies for Krakow and the Niepolomice Forest is available in Pazdur et al. (2013). The FFCO2 values for all the sites described above are given in Table SM3.

**Methods**

The PlastiGas sample bag was filled with air. The atmospheric CO2 was separated in the vacuum apparatus (**Figure 3**). The flowing air was dried by trapping the water vapor with a mixture of dry ice and alcohol at -80°C. The CO2 wasthen trappedwith liquid nitrogen (-196° C). The CO2 collection time was about 30 minutes. After reheating the trap, the CO2 was retrieved in a glass flask. The gas was subsampled with a syringe for 13C measurement by isotope ratio mass spectrometry (IRMS), and the remaining CO2 processed into graphite for the 14C isotope content determination by Accelerator Mass Spectrometry (AMS). The amount of recovered CO2 from the total volume of the air sample was sufficient to perform both types of isotopic analyses, i.e. equivalent to at least 1 mg of pure carbon.

**Fig. SM1.** The distribution of wind directions and frequencies for Gliwice city. Seasonal wind roses for the atmospheric CO2 sampling period from 26 January 2011 to 30 January 2013 for particular seasons and the total distribution for whole sampling period are presented. Data collected for the monitoring station in Gliwice, 2 km SW from CO2 sampling point (Voivodship Inspectorate of Environmental Protection, http://powietrze.katowice.wios.gov.pl/).

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**Fig. SM2.** Vacuum line for CO2 extraction from atmospheric air sampled in Gliwice. LN=Liquid Nitrogen.



**Table SM1** (in xls file) Results of 14C and 13C measurements of atmospheric CO2 in Gliwice and referenced calculations.

**Table SM2** (in xls file) Results of 14C and 13C measurements of pine tree rings from Gliwice surroundings and referenced calculations.

**Table SM3** Earlier measurement results of the Suess effect (FFCO2 value) for Southern Poland: Gliwice city, Silesia agglomeration, Krakow city and Niepołomice Forest (15 km in an easterly direction from Krakow). The FFCO2 values for some sites were estimated basing on published 14C data.

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| **City/region/sampling**  | **Year/Time span of measurements (yrs)** | **Mean value of FFCO2 (%)** | **Reference**  |
| Gliwice (1 sampling site, atm. CO2)  | January 1974 |  *ca* 5.8 | Awsiuk and Pazdur (1986) |
| Gliwice (1 sampling site, atm. CO2) | 1980 | *ca* 5.2 | *as above*  |
| Silesia agglomeration (5 sampling sites, atm. CO2) | 1980 | *ca* 5.5 | *as above* |
| Gliwice (1 sampling site, atm. CO2) | 1984 | *ca* 6.5 | *as above* |
| Ruda Sląska (1 site sampling site, tree rings measurements) | 1965-1995 | 3.64 ± 0.74 | Rakowski et al. 2001 |
| Chorzów(1 sampling site, tree rings measurements)  | 1966-1992 | 1.4 ± 0.9  | *as above* |
| Niepołomice Forest(4 sampling sites, tree rings measurements) | 1960-1980  | 0.60 ± 0.65 | Pazdur et al. 2007Pazdur et al. 2013 |
| Krakow(1 sampling site, tree rings measurements)  | 1983-2002 | 3.63 ± 0.27 | Rakowski et al. 2004 |
| Krakow(plants) | 1975-1976 | 4.5 to 5.6 | Florkowski and Kuc, 1979  |
| Krakow (1 sampling site, atm. CO2) | 1987-1994 | *ca* 4.9 | Kuc et al. 2007, Zimnoch et al. 2012,Pazdur et al. 2013 |
| Krakow (1 sampling site, atm. CO2) | 2000-2004 | *ca* 2.8 | *as above* |
| Krakow (1 sampling site, atm. CO2) | 2005-2009 | *ca* 3.4 | *as above* |